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Poling Dynamics and Effects of Trapped Charge in Poled Polymer Films for Nonlinear Optical Applications

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ABSTRACT

The behavior of surface and trapped charge that originates during contact electric-field poling of thin films of optically nonlinear polymers has been investigated. Thin films of polymethylmethacrylate doped with two different tricyanothiophene chromophores have been studied during and after the poling process by simultaneous measurement of the current through the poling circuit and the second harmonic generation signal (SHG) from the polymer system. The poling current present in a fresh sample was found to differ in both magnitude and temporal dependence to that observed in the sample during subsequent polings. The magnitude of the steady-state current eventually reached during the poling process was found to depend on temperature and was related to the mobility of charge. A sharp drop-off in SHG signal intensity occurring when the poling electrodes were grounded is considered to be due to the removal of surface charge that orients chromophore dipoles near the surface of the film; the decay in the macroscopic polarization that then occurs is prolonged by charges trapped in the polymer matrix. The build-up of trapped charge explains a memory effect in which the SHG signal relaxation time gradually increased as the film was subjected to multiple polings. Finally, it is demonstrated that the release of charges trapped in the polymer matrix depends upon the heating rate and continues far above the glass transition temperature of the polymer.

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INTRODUCTION

Due to qualities that distinguish them from currently-available, inorganic nonlinear optical (NLO) materials, much effort over the past decade has been directed towards the study of polymers combined with nonlinear optical chromophores for possible photonics applications.^{1,2,3} The most important advantages of polymeric NLO materials are low dielectric constants, high intrinsic nonlinearities, high damage thresholds, fast response times and ease-of-processability.^{4,5}

Second-order nonlinear optical processes are only active in materials that lack center-of-inversion symmetry. Electric-field poling has been the method of choice to remove the centrosymmetry from the inherently centrosymmetric polymeric NLO materials.^{6,7,8,9} Since the first report of organic NLO materials over 10 years ago,¹⁰ the majority of studies in this area have focused on one of two major areas: 1) the magnitude of the second-order response from NLO chromophore/polymer systems and its temporal stability,^{2,3,11,12,13} and 2) the physics of the orientation and relaxation processes that occur during poling and after the poling field has been removed.^{14,15,16,17} Although the presence of surface charge on poled NLO films has been discussed somewhat in the literature, particularly with regards to corona poling,^{18,19,20,21} little direct attention has been paid to the poling process itself and to the possible effects that *injected* charge has on the NLO behavior of these polymers. However, this area is of potential great importance as the poling an NLO film involves subjecting the polymer sample to a high electric potential thereby producing an electret.^{22,23,24}

In this report we continue our recently initiated examination²⁵ of the extent of the effects of residual charge on the NLO properties of these materials. In particular, in this study we wish to examine the charge effects in relation to second harmonic generation (SHG) signal behavior in representative large $\chi^{(2)}$ systems as compared with the previous model system of *para*-nitroaniline (*p*NA) in polymethylmethacrylate (PMMA).²⁵ The chemical structures of the components of the systems with which we chose to further examine these charge effects are shown in Fig. 1. Using the technique of hyper-Rayleigh scattering, the two tricyanothiophene chromophores shown have recently been shown to possess very large first hyperpolarizabilities,^{26,27} a preliminary attempt at measuring the χ_{333}^2 value of a 25 wt % chromophore-I/PMMA polymer film using the Maker Fringe method²⁸ indicates that it could be in excess of 50 pm/V.²⁹ By measuring the poling current and the SHG signal from the sample simultaneously we are attempting to elucidate the effects that charge has on the SHG signal, and its relaxation, induced by the electric poling field.

EXPERIMENT

For this study, polymethylmethacrylate (PMMA) combined with 25 weight per cent (wt %) "chromophore-I" and 5 wt % "chromophore-II" was used to form doped guest/host systems (Fig. 1). Very high molecular weight PMMA was obtained from Aldrich (catalog no. 18,226-5). The tricyanothiophene chromophores were synthesized in-house.³⁰ In order to remove possible low molecular weight impurities that might have affected the charging behavior of the polymer, some of it was "washed" before use. This

involved dissolving the polymer in a good solvent (chloroform) and then precipitating the polymer back out of solution by adding a nonsolvent (methanol). This washing step was repeated three times after which the precipitated polymer was dried under vacuum, first at 60 °C for 24 hours and then at 100 °C for at least two days. The temperature of glass transition (T_g) of the chromophore-II doped polymer was approximately 105 °C; T_g for the chromophore-I doped polymer was approximately 86 °C (as measured by a Perkin-Elmer Delta Series DSC-7 differential scanning calorimeter, heating rate 20 °C/min).

The preparation of the ITO sample substrates and chromophore/polymer/solvent (chloroform) mixtures and the spin-coating of thin-film samples were done as described previously.²⁵ (For purposes of comparison, NLO films were made from both washed and unwashed PMMA) Thin films of good optical quality and approximately 2 μm in thickness were prepared. To remove residual solvent, spun films were immediately placed into a vacuum oven heated to 75 °C (above the boiling temperature of chloroform); films were kept at 75 °C overnight without a vacuum applied and then for at least another 24 hours under vacuum. Using thermogravimetric analysis (TGA), this procedure proven to be very effective in removing all solvent from thin-film samples.³¹ No evidence of chromophore aggregation was visible in either the 25 wt % or 5 wt % films. To prepare a sample for use during experimentation, two slides were placed in contact with each other (film sides together) to form a "contact poling" configuration. This film "sandwich" was placed into a Teflon sample holder which was then mounted in a temperature-programmable (± 0.1 °C) sample oven. To insure good physical contact between the two films, the sample holder was designed so that pressure could be evenly applied to the

sample by tightening a set of four screws at the corners of the holder. Before experimentation began, the sample was fused by raising the temperature ($0.5\text{ }^{\circ}\text{C/min}$) in the oven to well above the T_g of the sample ($\geq T_g + 20\text{ }^{\circ}\text{C}$) for 10 hours and then slowly cooling the sample down ($0.5\text{ }^{\circ}\text{C/min}$) to the temperature of interest; the sample was then allowed an equilibration time of at least one hour before experimentation began. A sample heating/cooling rate of $0.5\text{ }^{\circ}\text{C/min}$ was chosen in this study as it is well known that rapid cooling (quenching) can distort the temperature of glass transition.³²

The experimental setup used during the course of this study has been described previously.^{25,33} Basically, the setup for SHG measurement consisted of a Q-switched Nd:YAG laser (Spectra-Physics GCR-11) operating at 10 Hz and the associated beam-conditioning optics. The fundamental light incident upon the sample was *p*-polarized; mixed polarized second harmonic light was detected. The incorporated poling circuit was designed to allow the poling electrodes to be shorted to ground upon poling termination. A Keithley model 6512 electrometer in its 200 nA range (resolution 10 pA) connected in series with the poling electrodes was used to detect the poling current. Data collection and analysis of both the SHG signal and the poling current was performed as previously described.²⁵

Three types of experiments were performed in this study. The first type was an isothermal poling/relaxation experiment in which the amount of elapsed time between polings was the parameter of interest. Here the sample was poled by applying a large voltage across the ITO electrodes (resultant electric fields were on the order of 2 MV/cm). The SHG signal was monitored and once it had reached a steady-state, plateau

level, the voltage was removed by grounding the electrodes. (Grounding the electrodes also served to remove charge from the electrode/polymer interface) The SHG signal was then monitored as it decayed away due to chromophore reorientation; at the same time, the current passing through the polymer was also measured. After the SHG signal decayed away completely, time was allowed to elapse and the process was repeated under identical experimental conditions (i.e. temperature, poling duration, maximum applied poling voltage). The second type of experiment was similar to the first except that in this case temperature was used as a parameter instead of elapsed time (i.e. isothermal poling/relaxation trials were performed over a range of temperatures). Prior to each measurement in this experiment, the sample went through an "erase" procedure that was designed to eliminate the thermal history of the sample. During this erase procedure, the sample was slowly heated ($0.5\text{ }^{\circ}\text{C/min}$) to a temperature of $T_g + 20\text{ }^{\circ}\text{C}$ where it remained for 1 hour before being slowly cooled down ($0.5\text{ }^{\circ}\text{C/min}$) to the temperature of interest. During the first poling of the sample (performed around the sample's T_g) the sample was poled until a steady-state SHG signal was obtained. To remove poling duration as a variable from subsequent measurements, this duration was then used at the other temperatures in the rest of the experiment.

The third type of experiment performed in this study was the simultaneous measurement of the SHG signal from, and the current through, a poled sample as the temperature was ramped from well below T_g to high above T_g . To prepare the sample for this measurement a poling voltage was first applied to the sample above T_g . The sample was poled at this temperature for a time sufficient to produce a steady-state SHG signal

before being allowed to cool at a constant rate to below T_g with the poling field still applied. Once there, the poling field was removed by grounding the electrodes which also served to remove surface charge. The sample was then heated at a constant rate to high above the glass transition temperature of the sample. During this heating process both the SHG signal and the current were monitored. The results from all three types of experiments are reported below.

In all the experiments described above, the poling voltage was not applied all at once to the sample. Instead the voltage applied was manually ramped in 10 or 20 V increments from 0 V to the maximum applied value (one increment approximately every 2 to 3 seconds) which was then maintained for the balance of the poling duration. This procedure was used as we have found that the sudden application of high voltage can result in early dielectric breakdown. The maximum applied voltage was the largest voltage resulting in a stable current of a few tens of nA through the sample. Throughout these experiments, there was no evidence of an abrupt increase in the SHG signal at the time of electrode grounding ("switching effect") nor was a sizable decrease in the SHG signal observed during long poling times as has recently been observed elsewhere.^{34,35}

RESULTS AND DISCUSSION

Shown in Fig. 2 is the poling current measured in a 5 wt % chromophore-II/(unwashed) PMMA sample at 115 °C (above the T_g of the polymer). During the poling process, the voltage was incrementally applied to the sample as explained above (maximum poling voltage was 470 V). As can be seen in the current trace, the current through the sample increased with each step increase in the poling voltage. [Also visible

in the figure are very fast transient currents that are the result of the sudden increases in voltage; they are not of interest here] It can be seen in the figure that after the poling voltage had reached its maximum level (indicated by the solid vertical line at 158 sec), the current through the sample began to slowly decrease before reaching a steady-state value after approximately 500 seconds. Also shown in the figure is the SHG signal from the sample measured at the same time as the current. One notes that in the beginning, the SHG signal slowly increased with poling potential at low voltages and then increased dramatically after the poling voltage reached a certain value. Of particular interest in this figure is the fact that at the time the current began its slow decay, the SHG signal had reached its maximum value and stayed relatively constant from then on. After this sample had been completely poled (for an appropriate poling duration as determined by the constancy of the poling current and the SHG intensity), the poling field was removed by grounding the electrodes. The SHG signal then decayed as a result of chromophore reorientation and polymer relaxation (*c.f.* Figs. 4 and 5). Data qualitatively similar to that shown in Fig. 2 was obtained from samples in which the polymer had been washed and also in experiments in which the temperature was held below the T_g of the material.

As shown in Fig. 2, when a high voltage is applied to an NLO film in order to orient the NLO chromophores, a small current through the sample is readily observed. Two sources of current are possible, their relative magnitudes depending upon the strength of the applied field. First, current can arise due to the orientation of molecular dipoles in the polymer matrix. By the continuity equation, a current density arises whenever polarization, \vec{P} , is time dependent. An applied electric field will cause the molecular

dipoles in the polymer matrix to orient along the field direction, resulting in \bar{P} becoming time dependent and a polarization current being generated. The inverse effect, the reorientation of dipoles back to their unpoled state upon the removal of the field, also results in a current for the same reason. These polarization and depolarization currents are well-known phenomena and have been extensively used in the literature in the study of polymer molecular dynamics.^{36,37,38,39,40}

The second source of current through a polymeric material is conduction. Although the resistance of polymers is, in general, very large, it is not infinite. Thus, by Ohm's Law a current *through* the polymer must result whenever a voltage is applied. In "pure" polymer, conduction is known to proceed in one of two ways: by the movement of ionic impurities⁴¹ and by a energy band mechanism similar to that used to explain conduction in metals.⁴¹ When conduction occurs by the energy band mechanism, the possibility of charge-trapping arises.⁴² Actual materials contain structural imperfections and impurities which result in the creation of localized electronic states. If these electronic states are low enough in energy, charge traveling through the polymer matrix can become trapped, drastically interfering with the passage of injected current. Two general types of trapping sites can then be anticipated, their relative numbers depending upon the temperature at which the sample is held. Those of the first type are of low energy so that charge will not be able to easily escape once it is there. In this case charge is "deeply trapped" and can only escape if the system is heated to high temperature. In the second type, the trapping sites are of higher energy so that charge will be able to continue to diffuse through the polymer after the poling potential has been removed. Due to the "deep trapping" effect

the number of available trapping sites will decrease as charge migrates through the sample; assuming the applied potential is not changed, this will correspond to a decrease in observed current. However, it is also to be expected that with multiple polings or long poling times, the total amount of charge present in the sample will increase until a saturation level is reached. Conduction in molecularly doped polymers of the type used as transport layers for xerographic photoreceptors has recently been shown to occur through a hopping mechanism, in which charge is envisioned to hop among molecular dopants.^{43,44,45,46,47} The hopping is seen to occur in a distribution of states, the width of which is due to the variation in spacing between individual dopant molecules resulting in a variation in site energy at each individual molecule.⁴⁸ This type of doped polymer is similar in principle to those studied for NLO applications. Conduction in NLO doped polymers has also been recently studied by Pasmore, et. al.⁴⁹

Fig. 3A shows the same current as plotted in Fig. 2 (Trial 1) and also the poling current in the sample the second and third times (Trials 2, 3) it was poled under identical conditions (above T_g at 115 °C). In this figure, only the current measured after the poling voltage had reached its maximum value is shown. In these experiments, Trial 2 (3) was started only after the SHG signal induced in Trial 1 (2) was allowed to decay to a background level. (Note that a thermal erase between trials was *not* performed in this experiment) There are several interesting aspects to the data presented in this figure. First, the maximum current observed during the first poling of the sample was larger than that measured during subsequent polings. Second, after the sample had been poled once, the current through the sample reached a steady-state value much more quickly than in the

fresh sample. Third, the current behavior observed during the second and third polings (and all additional ones although they are not shown) was nearly identical. Fig. 3B shows the current observed in the same sample using an identical experimental procedure but at a temperature of 105 °C (around the polymer's T_g). (The trials at this temperature were actually performed before the ones at 115 °C with a thermal erase procedure being performed in-between) The behavior of the poling current is rather similar in this case to that above T_g although the magnitude of the effects are somewhat reduced due to the decreased conductivity of the polymer at lower temperature. Note that the trends presented here are qualitatively identical to those presented in our earlier work on the *p*NA/PMMA model system.²⁵

It is our hypothesis that the currents shown in Fig. 3 are primarily due to the charge trapping mechanism previously mentioned. This mechanism is consistent with the trends shown: When a sample is poled for the first time, all of the trapping sites are available and thus the current through the sample is large (beginning of Trial 1, Fig. 3A and 3B). However, as the trapping sites become occupied, the current through the sample gradually decreases (middle and end of Trial 1, Fig. 3A and 3B). During the time that elapses before the next poling, some of the nondeeply trapped charge, and also possibly some of the deeply trapped charge, would be able to diffuse out of the sample. When the poling field is applied again, it only takes a short amount of time for charge to occupy the trapping sites that had become available due to charge diffusion during the time between the two successive polings. As a result, a steady state current is achieved much more rapidly than during the initial poling (Trials 2, 3, Fig. 3A and 3B).

In passing, it should be noted that Zimmerman, et. al.³⁶ have also recently reported on poling currents obtained from a contact-poled NLO polymer film (resultant fields were on the order of magnitude of 0.4 MV/cm). They, too, observed an initial decrease in the poling current at short times which they attributed mostly to polarization mechanisms although they concluded that "conduction mechanisms [could] still contribute significantly at these [short] times."⁵⁰ Even though our results are qualitatively similar to Zimmerman's, we believe that the behavior shown in Fig. 3 is dominated by conduction mechanisms, not polarization, for the following reasons. First, as shown in Fig. 2, the SHG signal had reached its maximum value by the time the current began its gradual decrease, indicating that the NLO chromophores and polar segments of the polymer chains⁵¹ were already optimally oriented by this time and therefore polarization current from this source would be negligible. Second, the slow decrease in the poling current is observed both above and below T_g in approximately the same time scale (*c.f.* Fig. 3A and 3B). Due to the great increase in segmental mobility above T_g , the chromophores would be able to orient faster above T_g . If polarization mechanisms were indeed responsible for the behavior shown in the figure, one would expect to see a significant change in the relaxation time from above T_g (115 °C) to around T_g (105 °C), in contrast to the experimental result. Finally, the different current versus time behavior with successive polings that was observed would not be expected if these were polarization currents as the system was allowed to relax completely before the next poling was begun.

We take the data shown in Figs. 2 and 3 to be evidence that charge is being injected from the electrodes and trapped into the polymer matrix. Vestweber has also recently

reported similar charge injection, using ITO electrodes, in the course of designing polymer light emitting diodes (LEDs).⁵² The presence of charge in the matrix is expected to affect the physical properties of the polymer system. In particular, we are interested here in the effect that the injected charge has on the relaxation rate of the SHG signal induced by the electric poling field. Shown in Fig. 4 are four SHG signal relaxation curves from a single, fresh (i.e. previously unpoled) 5 wt % chromophore-II/(washed) PMMA film held at 105 °C (around the sample's T_g) and isothermally poled for 550 sec with a maximum voltage of 550 V; the SHG signal relaxation times for these curves are tabulated in Table 1. In this experiment, the sample was first subjected to the fusing treatment described in the EXPERIMENTAL section (equilibration time at 105 °C for this sample was approximately 5 hours). Then sequential poling/relaxation measurements (Trials 1 - 3), identical to those performed to acquire the data in Fig. 3, were made on the sample (the SHG signal from one poling was allowed to decay completely away before the next poling was begun). One notes that the SHG signal decay time for the previously unpoled sample (Trial 1) is shorter than for the second poling (Trial 2) which is, in turn, shorter than the decay time for the third (Trial 3). These results are similar to those reported earlier by our laboratory^{53,54,51} in that the first three isothermal polings show evidence of a "memory" effect in which the SHG signal takes progressively longer times to decay after each poling. It is our hypothesis that injected charge is responsible for this effect. After the first three relaxations were performed the sample was allowed to remain overnight at 105 °C and was then subjected to the thermal erase procedure described above. The sample was finally subjected to a fourth isothermal poling/relaxation cycle (Trial 4) using the same

parameters (temperature, poling field, duration of poling) as the first three. One notes that the result of Trial 4 does not mimic Trial 1 but is rather closer to Trial 2. (Trial 4 will be further discussed below).

Charge injected by the electrodes into the matrix could be responsible for the memory effect in several ways. That charge injected and trapped near the surface of the polymer film would create an electric field inside the polymer which would orient the dipoles in the same direction as the poling field. Charge in the bulk of the polymer would correlate the motion of chromophore dipoles. This correlation can be understood as follows: Since the effect of the poling field is to orient the NLO molecules so that their dipole moments point in the same direction, this would lead to unfavorable electrostatic interactions between neighboring chromophores. The presence of an appropriate charge between two chromophores would counteract this interaction. In addition, the presence of such a charge would force a chromophore-charge-chromophore system to behave as a unit. The combined mass and volume of such a unit would be much greater than a single chromophore thus hindering reorientation. As more and more charge is injected during subsequent polings, this charge injection scenario predicts that the SHG signal relaxation time will continue to increase until the polymer becomes saturated with charge, after which the relaxation time should remain constant as long as the charge saturation is maintained and no other mechanisms are present.

Physical aging, the process by which a polymer at or below T_g spontaneously loses free volume in its approach to thermodynamic equilibrium,⁵⁵ has recently been considered as the cause for an observed increase in SHG signal relaxation time at and below T_g during

sequential poling experiments.⁵⁶ However, we do not believe physical aging to be the cause of the lengthening effect observed here. First, during this experiment, the polymer was held around its T_g . It is well known that a polymer held at T_g obtains thermodynamic equilibrium very rapidly, on the order of one minute; for temperatures as low as $T_g - 5$ this time is only on the order of an hour.⁵⁵ Thus, in this case, any physical aging that occurred would have taken place during the time that the sample was allowed to thermally equilibrate before the first poling. Second, it is known that the physical aging process is thermoreversible, i.e. a brief excursion (e.g. 20 minutes) above T_g will cause the polymer to "forget" its thermal history, any previous aging it may have undergone below T_g having been erased.⁵⁵ The fourth isothermal poling of this experimental set (Trial 4, Fig. 4) demonstrates this. Since before this poling was performed the sample was heated up and held above T_g (125 °C) for over an hour, this would have erased the thermal history of the sample. If physical aging was indeed the cause of the memory effect, one would then expect the first and fourth SHG signal relaxations to have coincided which, as seen from the figure, is obviously not the case. As has been shown elsewhere^{25,40} charge trapped in a polymer sample is not completely released until it is heated *far* above its T_g . Thus, it is our hypothesis that the reason the relaxation of Trial 4 is different from that of Trial 1 is that enough trapped charge remained after the thermal erase procedure to affect the rate of the relaxation. It is interesting to note that Schüssler, et. al. used a thermal erase procedure similar to that reported here and obtained excellent reproducibility between poling trials.^{34,35} The temperature to which their samples were heated (approximately $T_g + 100$ °C), however, was much higher than the $T_g + 20$ °C used here. It is likely that heating to

this high a temperature allowed complete removal of all injected charge from their samples, as we shall also describe below.

As the SHG signal decays were not, in general, single exponential, we fit our data to the Kohlrausch-Williams-Watts (KWW) stretched exponential equation using an optimized in-house fitting program.⁵⁷ The KWW equation is commonly used to describe relaxations occurring in complex systems.^{58,59,60} Using this equation, the decay of the SHG signal from the time the poling voltage is removed from the sample can be characterized by an average relaxation time, $\langle \tau \rangle$:

$$\langle \tau \rangle = \int_0^{\infty} \exp\left(-\left(\frac{t}{\tau_0}\right)^{\beta}\right) dt = \frac{\tau_0 \Gamma\left(\frac{1}{\beta}\right)}{\beta}. \quad (1)$$

The measured intensity of the second-harmonic light, I_{SHG} , is directly proportional to $|\chi^{(2)}|^2$, where $\chi^{(2)}$ is the second-order nonlinear susceptibility of the polymer system.⁶¹

The time dependence of the $\chi^{(2)}$ decay is assumed to be given by the KWW equation as

$$\chi^{(2)} \propto \sqrt{I_{SHG}} = ae^{-\left(\frac{t}{\tau_0}\right)^{\beta}}. \quad (2)$$

Here τ_0 is the characteristic relaxation time, a is the signal amplitude, β is the width parameter (often interpreted as describing a distribution of relaxation times) whose value is $0 < \beta \leq 1$ and Γ is the gamma function. (Note that if β is unity then the decay is single exponential)

Tables 1 - 4 present fitting results for SHG signal relaxations from different samples, with different poling times and at temperatures at and above T_g . It should be noted that for the data presented in these tables, χ^2 (chi squared), which is an indication of the goodness-of-fit and which should not be confused with $\chi^{(2)}$ in Eqs. (1) and (2) above, was always ≥ 0.997 , indicating very accurate fits to our data. In these tables "Elapsed Time" refers to the amount of time from the beginning of the first poling/relaxation trial of the cycle and "Time Between Polings" refers to the amount of time that passed from the beginning of one poling/relaxation trial to that of the next. Note in the tables that if the Elapsed Time resets to zero (e.g. Tables 1 and 2) this indicates that the sample was subjected to a thermal erase procedure between that poling/relaxation and the previous one. Note also that in all the tables the τ column refers to the single exponential relaxation time [i.e. in the fitting program, the β parameter of Eq. (1) was forced to unity] and that β and $\langle\tau\rangle$ are the width parameter and the average relaxation time, respectively, given in Eqs. (1) and (2) above.⁶² The τ column is presented as for this data, fitting to Eq. (2) often resulted in $\beta > 1$.

From an overview of the tables, it can be clearly seen that the trend of relaxation time elongation exhibited in Fig. 5 is reproducible between different samples. It is also interesting to note that the relaxation time elongation occurs even above the glass transition temperature of the polymer (Table 4) although the effect is not as pronounced as it is around T_g (Tables 1 - 3). In Table 4 one notes that the relaxation rate reaches a steady-state of around 195 secs after the fourth poling where it maintains for two further polings. Apparently after the fourth poling the polymer had become saturated with charge

as the relaxation rate reached a steady-state. Comparing the data in Tables 1 and 2, one notes that the relaxation times τ and $\langle\tau\rangle$ are consistently longer for the sample prepared with washed PMMA than they are for the sample prepared with unwashed PMMA. This is due to the plastization effect of small molecular impurities that are removed by the washing procedure apparently have important effects in shortening the relaxation time. This plastization effect is similar to that found in translational diffusion as investigated by the holographic grating technique.⁶³

It is interesting to note that a similar "memory effect" in a polymer above its T_g has recently been reported in the literature by Schüssler, et. al.⁶⁴ In this study, the authors compared the rate of SHG signal *recovery* after allowing their poled polymer to relax to varying degrees. They found that the rate of SHG signal recovery decreased as the delay between the removal of the poling voltage and its reapplication during the next poling increased. They attributed this decrease to long-range structural relaxations, the existence of which in the viscoelastic regime of polymers is currently being debated,⁶⁵ although they admitted that they had no rigorous proof in favor of this explanation. However, our scenario of charge injection can be used to explain their results. For the same reasons that charge injection would slow down SHG signal decay, it would speed up SHG signal recovery. As more time was waited between polings, more charge would have been able to escape from the polymer, thus slowing down SHG signal recovery.

Also of interest in Tables 1-3 is the behavior of the β parameter. As a general trend it can be clearly seen that the β parameter decreases with each poling/relaxation cycle. (In these tables this decrease occurs starting with $\beta > 1$; although in the KWW formalism $\beta >$

1 has no meaning, for these data, the trend persists). In the literature, a decrease in β has been taken to indicate that a broader distribution of relaxation times has to be included to adequately describe the relaxation.⁶⁶ The decrease in β indicates that the injection of charge into the system causes the dopant chromophores to experience larger regions of the inhomogeneous environment within the polymer.

Not only can injected charge influence the behavior of the SHG signal, but charge residing on the surface of the polymer film (at the polymer/electrode interface) (*surface charge*) or near the surface of the polymer film can affect the signal as well. Shown in Fig. 5 is a plot of the SHG signal from a 5 wt % chromophore-II/PMMA sample poled at 105 °C for 955 sec with a voltage of 470 V before and after the poling electrodes were grounded. Also shown is the current measured in the poling circuit during this time. As can be seen from the figure inset, at the moment the electrodes are grounded, a "spike" is observed in the current trace; at the same time, the SHG signal takes a step decrease (approximately 5 % in this case). This behavior can be understood as the response of the NLO chromophores residing on the surface of the polymer. Due to the presence of surface charge, these surface chromophores will be oriented to a larger degree than those in the interior (as they are less restricted) and will thereby contribute to a larger extent to the overall SHG signal.⁵ However, as soon as the surface charge has dissipated after the poling electrodes are grounded, these surface molecules are then free to relax. The rate at which they do so thus depends upon how quickly the surface charge is dissipated. As can be seen from the inset in the figure, this dissipation occurs very rapidly (the current has reached a zero value after approximately 0.1 sec). Thus, the step decrease in the SHG

signal at the time of electrode grounding can be explained by the disorientation of surface dipoles. However, as has been shown elsewhere,⁵³ the rate of the step drop-off can be slowed down by increasing the resistance in the poling circuit.

Such a step-decrease in SHG signal at the time of electrode grounding has also been noted by Dhinojwala, et. al.⁶⁷ However, they interpreted the effect as being due to the removal of the DC field-induced third order nonlinearity, which was estimated to be between 5 % and 10 % of their total SHG signals. Although this effect must be present to some degree in our system as well, it is not clear that this third-order nonlinearity is the dominant cause here. First, in both this study and the previous one,²⁵ the magnitude of the step drop-off was not the same for all relaxations with a given sample under the same experimental conditions and varied by as much as 2 or 3 % of the total. In contrast, one would expect a constant value for the contribution of the third order effect under such conditions. More interesting is a comparison of the magnitude of the step drop-off in this study and that observed in the previous *p*NA/PMMA system where it was as high as 50 % of the total SHG signal. The surface-charge scenario is consistent with the fact that *p*NA molecules are much smaller than the tricyanothiophene molecules investigated here and could thus disorient more quickly. Additionally, the fact that the step drop-off can be controlled by changing the external resistance of the connections to the poling electrodes (as mentioned above) also favors the surface dipole reorientation mechanism.⁵³

The effect of temperature on the poling current through the polymer is demonstrated in Fig. 6. Shown here are the isothermal poling currents through a 5 wt % chromophore-II/(washed) PMMA sample poled with a potential of 550 V at temperatures ranging from

105 °C to 122.5 °C (measurements were also made at other temperatures not shown in the figure). Each trace in the figure shows the current through the sample after the poling voltage reached its maximum value. Prior to each measurement the sample was subjected to a thermal erase procedure as described above. As expected, the magnitude of the steady-state poling current increases with increasing temperature. Also observable at the beginning of each trace is the polymer charging effect (*c.f.* Fig. 3). One notes that as the temperature increases, the current becomes increasingly unstable, exhibiting rapid fluctuations of 100 nA or more (*c.f.* the current at 122.5 °C); if allowed to continue these would eventually lead to dielectric breakdown. Thus, the measurement of the current through the sample is important in determining the upper temperature boundary for high-field isothermal poling.

Fig. 7 is an Arrhenius plot of the temperature-dependent relaxation time data obtained by fitting the SHG signal relaxation curves taken at the different temperatures; the data is also summarized in Table 5. Over the somewhat limited temperature range in which the data were taken ($T_g - 2.5$ °C to $T_g + 20$ °C), the data clearly follow Arrhenius-like behavior with a calculated activation energy of 254 kJ/mole. This result is consistent with that obtained earlier by King and Singer⁶⁸ and recently by Schüssler, et. al.³⁴ in guest/host NLO systems.

Figs. 8 and 9 show the measurement of the SHG signal and the current associated with the release of trapped charge from a 5 wt % chromophore-II/(washed) PMMA polymer sample as the sample was heated to far above the polymer's glass transition temperature. In these experiments, the sample was first heated to 120 °C. A poling

voltage of 500 V was then (incrementally) applied to polarize the sample. After achieving a steady-state SHG signal, the sample was allowed to cool at a rate of 0.5 °C/min, with the poling field still applied, to 45 °C.⁶⁹ Once the sample reached 45 °C, the poling field was removed by grounding the poling electrodes. The sample was then heated (at a rate of 0.25 °C/min, Fig. 8, and at a rate of 0.75 °C/min, Fig. 9) to well above the glass transition temperature. During heating, both the current flowing through the sample and the SHG signal were continuously monitored (note that no voltage was applied during this time). It is interesting to note that on slow heating (0.25 °C/min, Fig. 8), the SHG signal intensity decreases gradually until about 100 °C, after which it takes a precipitous drop to the background level around 115 °C. On more rapid heating (0.75 °C/min, Fig. 9), the SHG intensity decreases only slightly up to 100 °C, beyond which it also drops precipitously to the background level around 115 °C. Since the decrease of the SHG intensity is associated with the randomization of the dipole orientation, one would expect rapid heating to cause the SHG intensity decrease to occur at a lower temperature, in contrast to the experimental result shown in Fig. 8. In guest/host polymer systems, the orientational motion of the NLO chromophores is closely coupled to the movement of the polymer main chains: the precipitous decrease of the SHG intensity in the temperature range between 100 and 115 °C is clearly associated with the onset of the large-scale α -relaxation responsible for the glass transition.⁷⁰ Evidently, the detailed behavior of the SHG intensity decrease below T_g is intimately related to the balance between chromophore reorientation and conductivity of thermal energy in the whole NLO polymer system. Apparently a considerable time duration is needed for the chromophores to acquire

thermal energy from heating. At 0.75 °C/min, the heating rate is probably too fast for the chromophores to randomize their orientation, whereas at 0.25 °C/min there is enough time for the sample to achieve a thermal energy redistribution so that orientational randomization can occur at lower temperatures.

The behavior of charge flowing out of the sample also depends (strongly) on the heating rate. When the sample was heated slowly, at a rate of 0.25 °C/min (Fig. 8), the magnitude of the current increased steadily from the beginning of heating and reached a maximum around 85 °C (which is below the T_g of the polymer). The magnitude of the current then decreased and reached a plateau around 115 °C. This same current level maintained until around 150 °C beyond which the current went through a second decrease. When the polymer was heated more rapidly, at a rate of 0.75 °C/min (Fig. 9), the magnitude of the current increased steadily from nearly the beginning of the temperature ramp, reaching a maximum around the T_g of the polymer and then maintaining a nearly steady-state level after that.

As discussed above, charge injected into the system will be trapped to different extents (i.e. shallow and deep trapping) but will diffuse out of the polymer at a rate that depends upon the material's inherent charge-storage capacity and its bulk resistivity.⁴¹ The application of energy (heat) to the system will naturally accelerate this diffusion process. One would then expect that at a low enough heating rate, charge diffusion would occur at lower temperatures for the same reason as given for the SHG signal intensity decrease under the same conditions. Thus, in our experiments, when the heating rate was slow (0.25 °C/min, Fig. 8), there was enough time for the nondeeply trapped charge to

diffuse out of the polymer on its own accord; i.e. the natural rate of diffusion of this charge was faster than the heating rate. This diffusion of nondeeply trapped charge is probably the origin of the current plateau that occurs below T_g in Fig. 8. However, more deeply trapped charge requires application of energy to be removed and was therefore not released until above the polymer's T_g ; this is the origin of the second current plateau in the 0.25 °C/min measurement. With a faster heating rate (0.75 °C/min, Fig. 9) charge is forced out of the polymer sample more quickly. In this case, the diffusion of nondeeply trapped charge and deeply trapped charge overlap each other and a continuous band is observed as shown in Fig. 9.

One notes in Figs. 8 and 9 that the current resulting from the diffusion of injected charge had not gone completely to zero by 160 and 170 °C, the temperatures at which the respective experiments were stopped. Our samples decomposed at temperatures above 170 °C so this was our temperature limit. However, if special care had been taken to conduct the experiments in an inert atmosphere to avoid oxidation of the polymer samples, one would expect the current to have decayed to a zero value as the temperature was raised further and as all the charge trapped in the polymer was released. However, as the instrumentation necessary to perform this experiment is rather elaborate, it was not carried out in the present study. It is possible that part of the current measured during the time of the SHG signal intensity (Figs. 8 and 9) decrease is depolarization current. However, as pointed out in our earlier work,²⁵ and as consistent with the theoretical analysis of Köhler, et. al.,⁴⁰ the magnitude of the depolarization current depends on the heating rate. If the heating rate is small compared to the dipolar reorientation rate, as was the case here, then

only a small depolarization current will be detected as there is then is sufficient time for the dipoles in the sample to achieve partial uniformity.

SUMMARY AND CONCLUSIONS

To summarize, we have carried out a detailed investigation into the behavior of surface and trapped charge in thin films of a guest-host, nonlinearly-active polymer. We have shown that as a polymer sample is poled for the first time, the current through the sample is very large but gradually decreases to a plateau level. When the sample is poled again after its initial, first poling, the current through the sample starts out at a much lower level and more quickly reaches the plateau level. We have attributed these results to and to the accumulation of charge which is injected into the sample. Furthermore, we have confirmed the gradual lengthening of the SHG signal relaxation time as the polymer film is successively poled and have provided evidence to associate this "memory" effect with the poling current and to the accumulation of trapped charge in the polymer matrix.

By studying the current through the samples during the poling process, we have found that the plateau current depends on temperature and is related to the mobility of the charge. By simultaneously monitoring the current through the sample and the SHG signal from the sample, we have been able to show that the drop-off in the SHG signal is strongly correlated to the removal of surface charge. We have attributed the sharp decrease in the SHG signal to the reorientation of NLO chromophores near the surface of the sample. The slow decay of the remaining SHG signal has been associated with the relaxation of the chromophore dipoles oriented in the interior of the sample. The reorientation of these chromophores has been shown to be greatly retarded by the

presence of trapped charge. Finally, we have shown that release of trapped charge depends upon heating rate and that charge continues to be released high above the glass transition temperature of the sample after the SHG signal has decayed completely away.

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Table 1 - 5 wt % chromophore-II/(washed) PMMA
 Poling/Relaxation Trials at 105 °C
 Poling Potential: 550 V
 Poling Time: 560 sec

Trial Number	Elapsed Time (min)	Time Between Polings (min)	τ (sec)	β	$\langle \tau \rangle$ (sec)
1	0	--	2079	1.26	1807
2	104	104	2978	1.02	2927
3	289	185	5056	0.89	5664
4	0	--	3066	1.06	3003

Table 2 - 5 wt % chromophore-II/(unwashed) PMMA
 Poling/Relaxation Trials at 105 °C
 Poling Potential: 500 V
 Poling Time: 563 sec

Trial Number	Elapsed Time (min)	Time Between Trials (min)	τ (sec)	β	$\langle \tau \rangle$ (sec)
1	0	--	520.0	1.03	512.8
2	78	78	564.0	0.94	582.5
3	163	85	676.6	0.88	731.3
4	247	84	562.6	0.85	618.3
5	323	76	525.1	0.83	583.4
6	0	--	524.6	0.88	565.1
7	95	95	612.1	0.75	742.4
8	185	90	595.4	0.70	759.9

Table 3 - 5 wt % chromophore-II/(unwashed) PMMA
 Poling/Relaxation Trials at 105 °C
 Poling Potential: 470 V
 Poling Time: 950 sec

Trial Number	Elapsed Time (min)	Time Between Trials (min)	τ (sec)	β	$\langle \tau \rangle$ (sec)
1	0	--	1014.9	1.19	933.6
2	123	123	1402.1	1.01	1391.3
3	223	100	1582.2	0.99	1598.7
4†	1463	1240	3068.2	1.24	2928.0

†Overnight poling - In this case the same was poled from 10:30 p.m. to 10:30 a.m. the following morning (at 470 V)

Table 4 - 5 wt % chromophore-II/(unwashed) PMMA Poling/Relaxation Trials at 115 °C
(above T_g)

Poling Potential: 470 V

Poling Time: 605 sec

Trial Number	Elapsed Time (min)	Time Between Trials (min)	τ (sec)
1	0	--	178.2
2	38	38	188.2
3	80	42	189.7
4	128	48	196.7
5	166	38	193.5
6	194	28	194.1

Table 5 - 5 wt % chromophore-II/(unwashed) PMMA

Poling/Relaxation Trials from 102.5 °C to 125.0 °C

Poling Potential: 550 V

Poling Time: 560 sec

Temp (°C)	τ (sec)	β	$\langle \tau \rangle$ (sec)
102.5	5154.3	1.31	4423.1
105.0	3066.1	1.05	2938.0
107.5	2388.6	0.94	2421.3
110.0	1609.9	1.04	1552.0
112.5	865.5	1.02	853.6
115.0	513.2	1.10	482.7
117.5	311.8	1.16	306.5
120.0	190.4	1.11	189.3
122.5†	106.8	1.14	105.4
125.0†	58.9	1.11	56.3

†For these two (high) temperatures highlighted, the current was too unsteady to allow the full 560 sec of poling time. At 122.5 °C, the poling time was 382 sec; at 125.0 °C the poling time was 454 sec.

FIGURE CAPTIONS

Figure 1 - Chemical structures of the nonlinear optical tricyanothiophene chromophores and polymer used during the course of this study. The IUPAC names of the two tricyanothiophene chromophores are (E)-[5-[2-[4-(diethylamino)phenyl]ethenyl]-2-thienyl]ethenetricarbonitrile (chromophore-I) and (E)-[5-[2-[4-(diphenylamino)phenyl]ethenyl]-2-thienyl]ethenetricarbonitrile (chromophore-II).

Figure 2 - SHG signal and current data during first poling at 115 °C of a 5 wt % chromophore-II/(unwashed) PMMA sample; the maximum applied voltage of 470 V was applied gradually in 20 V increments. The solid vertical line is meant as a guide to the eye and indicates that the SHG intensity had reached its maximum value at the time the current began its slow decay. Visible at the beginning of poling are transient current “spikes” that are due to sudden increases in the applied voltage.

Figure 3 - Plot A) Poling current through a 5 wt % chromophore-II/(unwashed) PMMA sample during its first three polings at 115 °C; only the current after the poling potential reached its maximum value is shown. Plot B) Poling current through the same 5 wt % chromophore-II/(unwashed) PMMA sample during its first three polings at 105 °C; only the current after the poling potential reached its maximum value is shown.

Figure 4 - Demonstration of the elongation of SHG signal relaxation time during subsequent isothermal poling/relaxations of a 5 wt % chromophore-II/(washed) PMMA sample at 105 °C (around T_g). Experimental conditions were exactly the same for each measurement [temperature, maximum applied poling potential (550 V) and poling duration (550 sec)] Before Trial 1, the sample had been previously unpoled. The

relaxation times presented in the inset were obtained by fitting the raw SHG intensity data to Eq. 2a with $\beta = 1$. The data of each trial has been normalized.

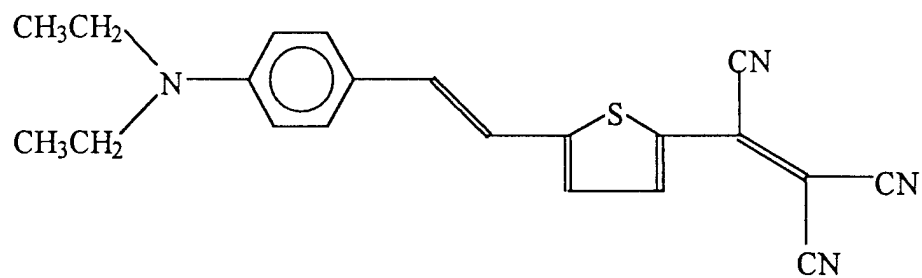
Figure 5 - Demonstration of the step drop-off in the SHG signal from a 5 wt % chromophore-II/(unwashed) PMMA sample at the time of poling electrode grounding; in this example, the drop-off is approximately 5 % of the total signal. Inset: Observation of the “spike” in the electrode current at the time of electrode grounding. The spike and the step drop-off in SHG signal coincide. If the current spike is viewed on an expanded scale (not shown) it can be seen that the surface charge is removed in approximately one-tenth of a second. The SHG signal has been normalized.

Figure 6 - The effect of temperature on the poling current through a 5 wt % chromophore-II/(washed) PMMA sample; only the electrode current after the poling voltage had reached its maximum level is shown. Measurements were taken at 105 °C (closed circles), 107.5 °C (closed squares), 110 °C (closed “up” triangles), 115 °C (closed “down” triangles), 117.5 °C (closed diamonds), 120 °C (closed hexagons) and 122.5 °C (open circles). For the measurement at 112.5 °C, the poling current underwent rapid fluctuations of more than 100 nA (some of this fluctuation was larger than the scale of the figure) and poling had to be terminated before completion in order to prevent dielectric breakdown in the sample.

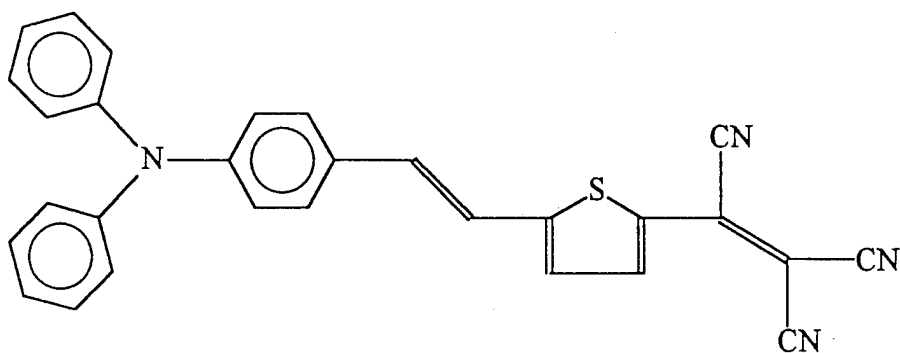
Figure 7 - Arrhenius plot of the KWW-derived SHG decay rate constant data for a 5 wt % chromophore-II/(washed) PMMA film. From this plot an activation energy of -254 kJ/mole was calculated.

Figure 8 - Normalized SHG signal and current from a poled 5 wt % chromophore-II/(washed) PMMA film as it was heated at a rate of 0.25 °C/min from 45 °C to approximately 160 °C. Poling of the film began at 120 °C (above T_g) and the film was allowed to cool, with the field still applied, to the starting temperature.

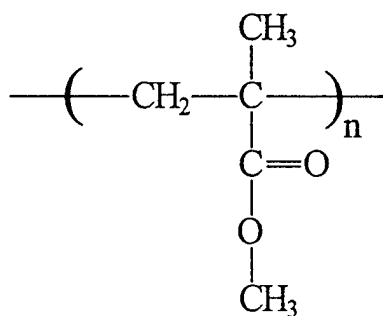
Figure 9 - Normalized SHG signal and current from a poled 5 wt % chromophore-II/(washed) PMMA film as it was heated at a rate of 0.75 °C/min from 45 °C to approximately 170 °C. Poling of the film began at 120 °C (above T_g) and the film was allowed to cool, with the field still applied, to the starting temperature.



“Chromophore-I”



“Chromophore-II”



polymethylmethacrylate
PMMA

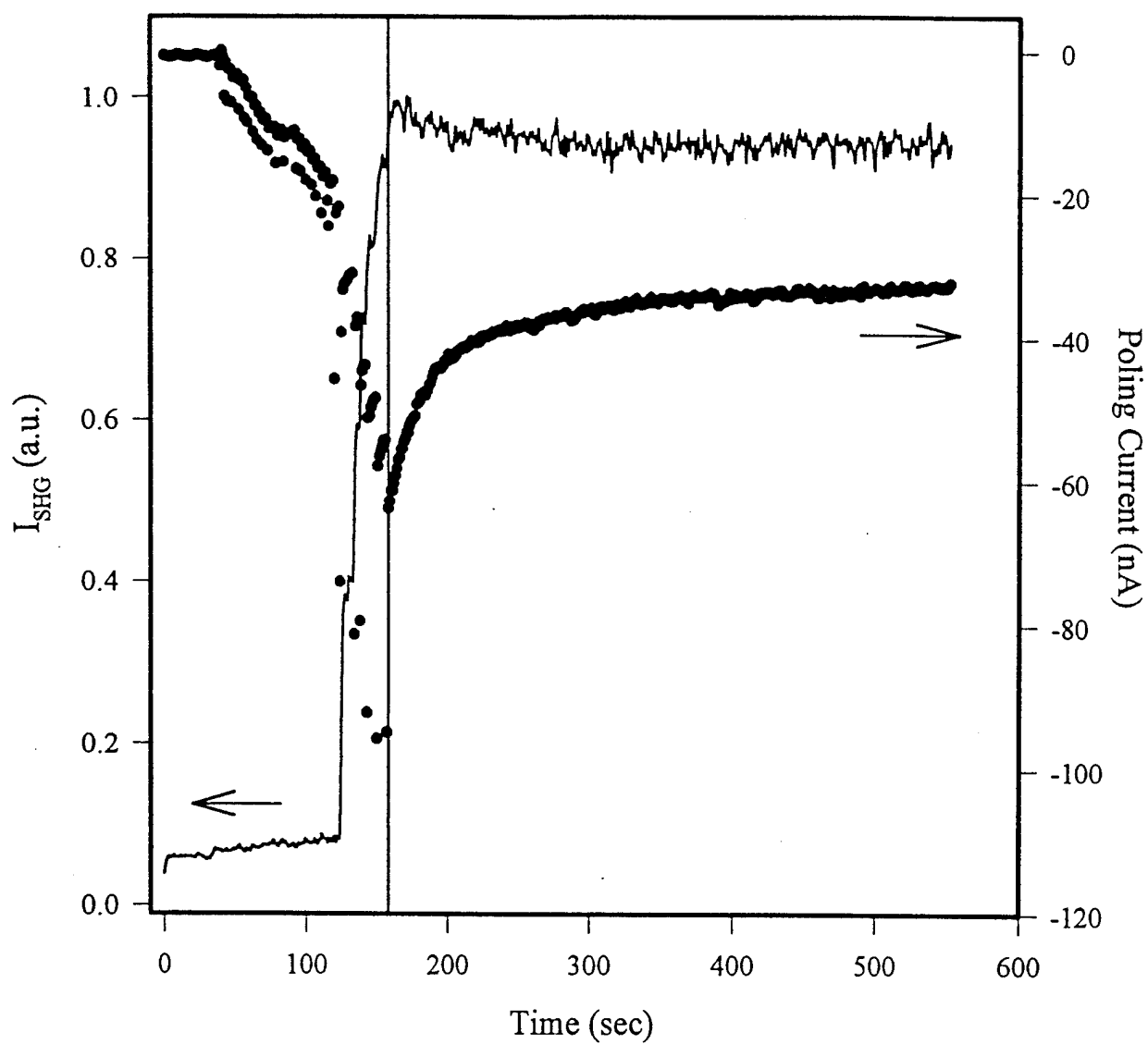


Figure 2, M. A. Pauley, *Macromolecules*

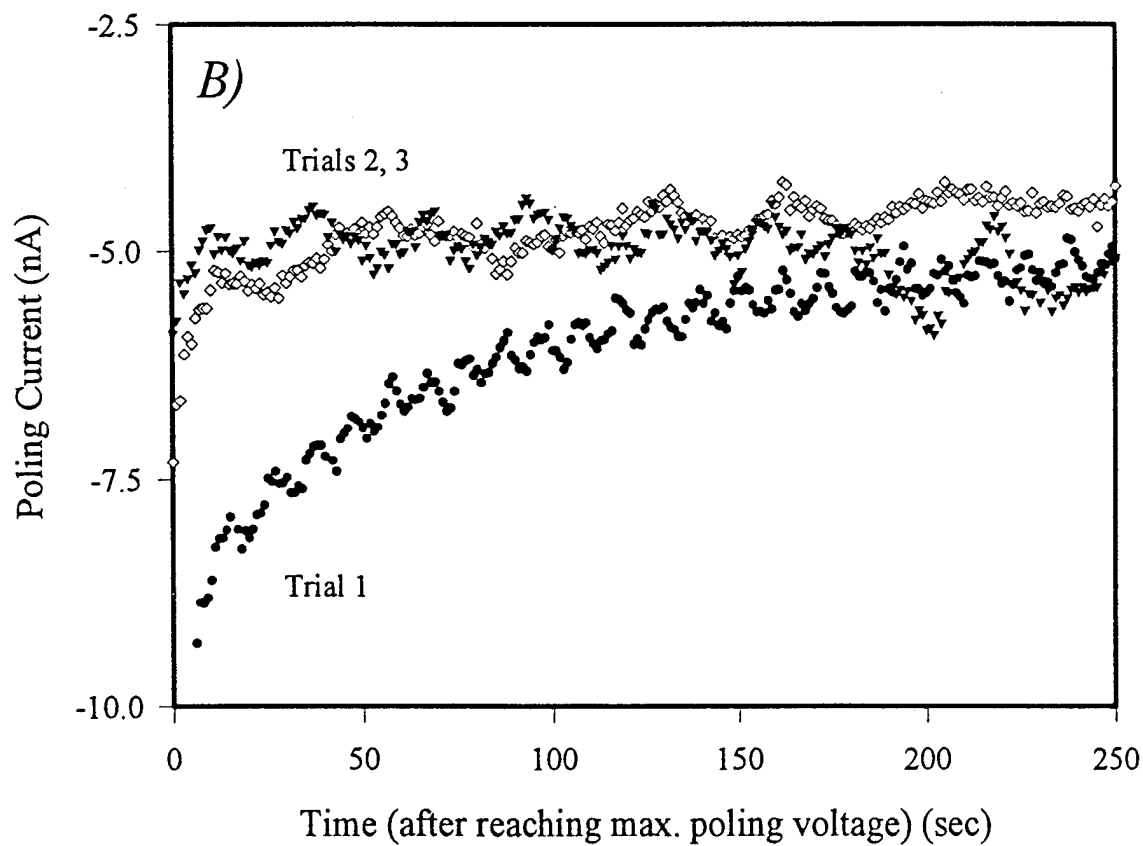
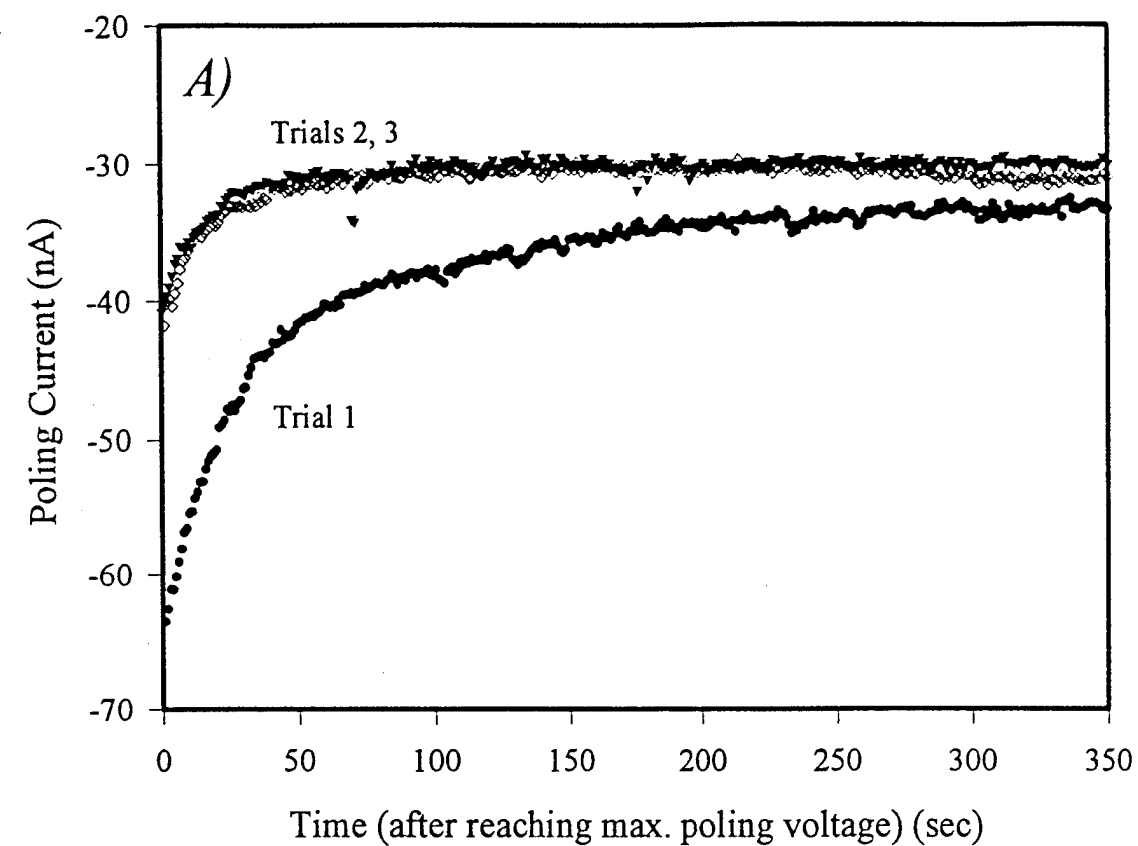


Figure 3, M. A. Pauley, *Macromolecules*

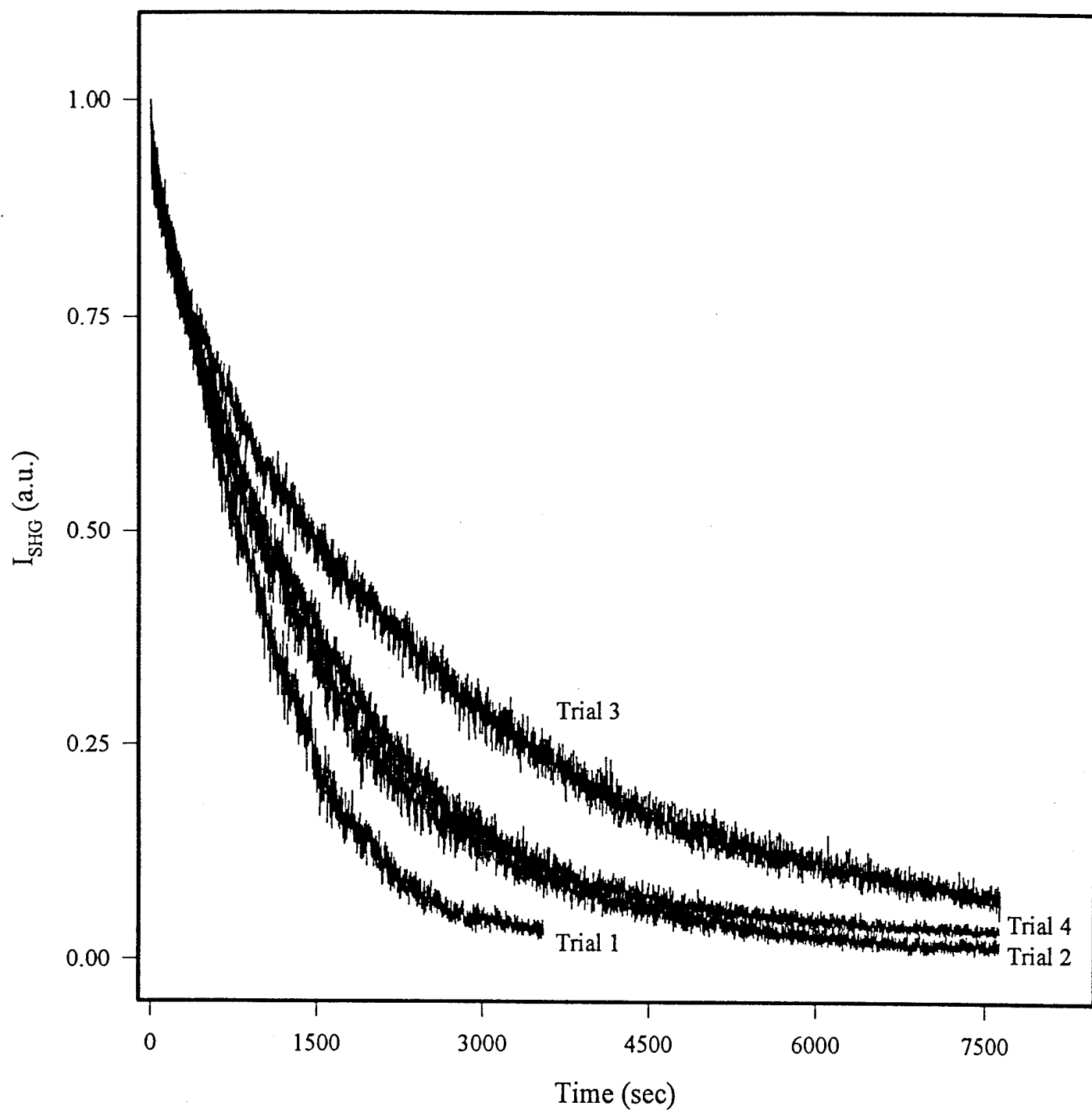


Figure 4, M. A. Pauley, *Macromolecules*

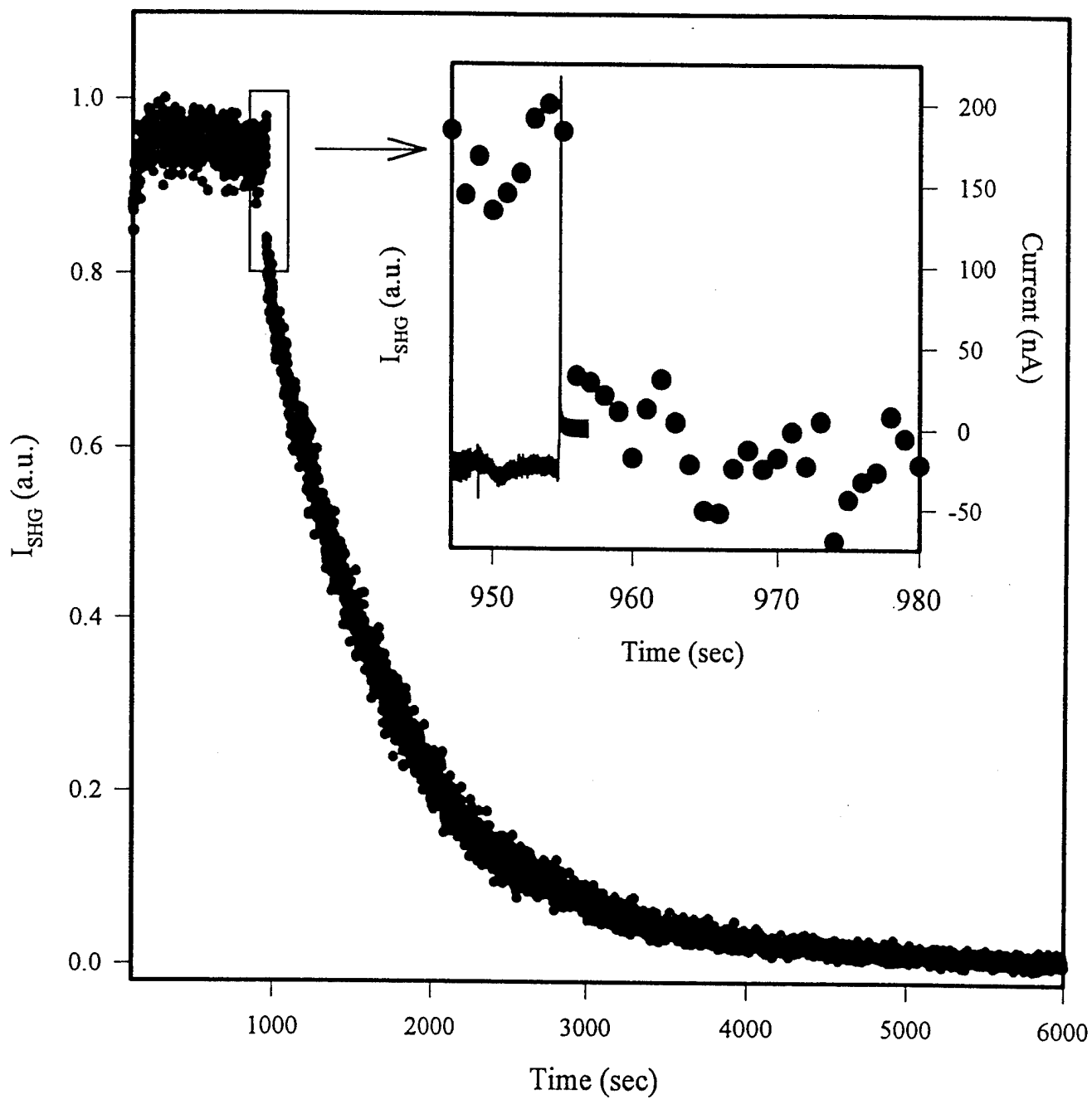


Figure 5, M. A. Pauley, *Macromolecules*

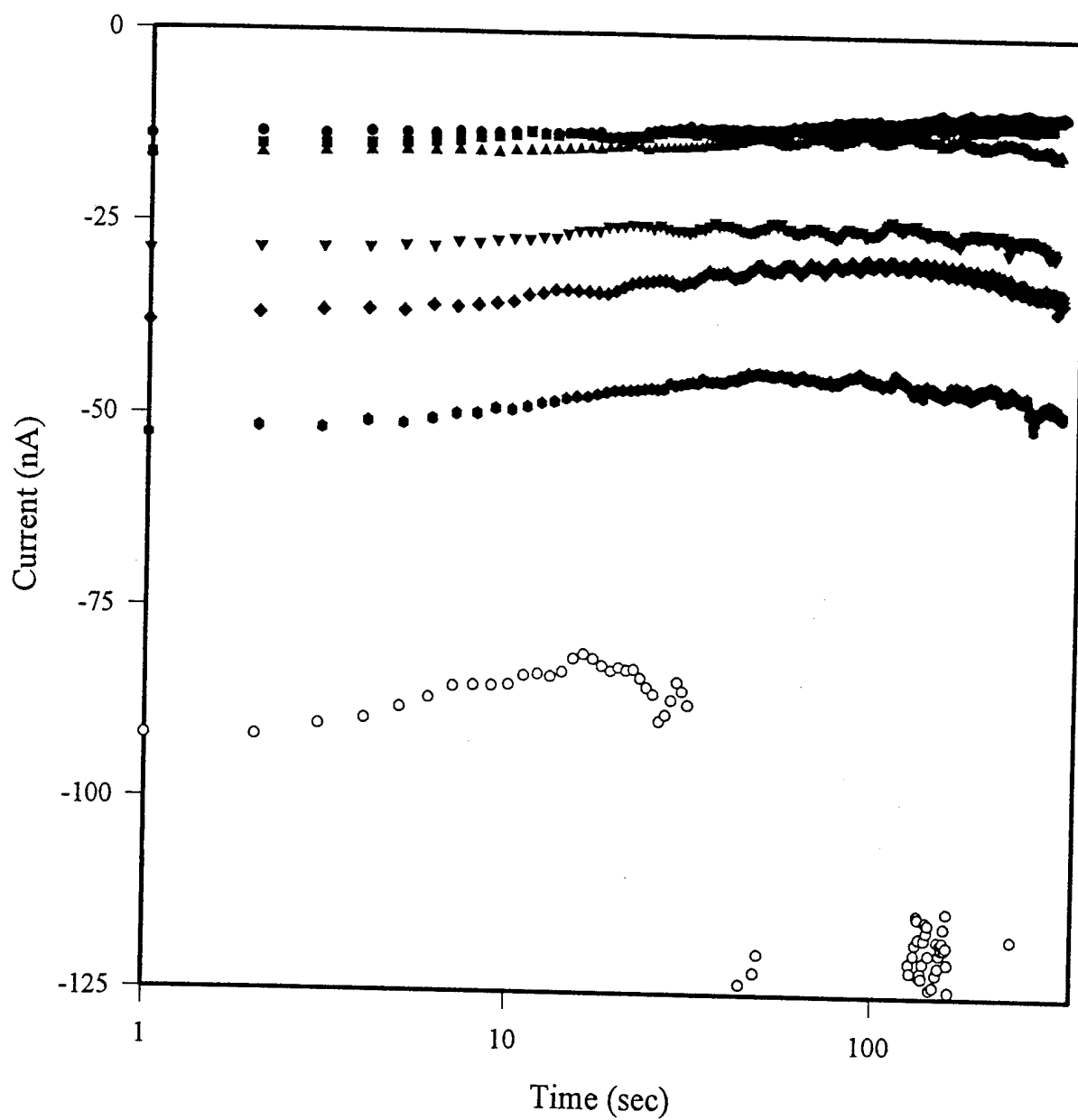


Figure 6, M. A. Pauley, *Macromolecules*

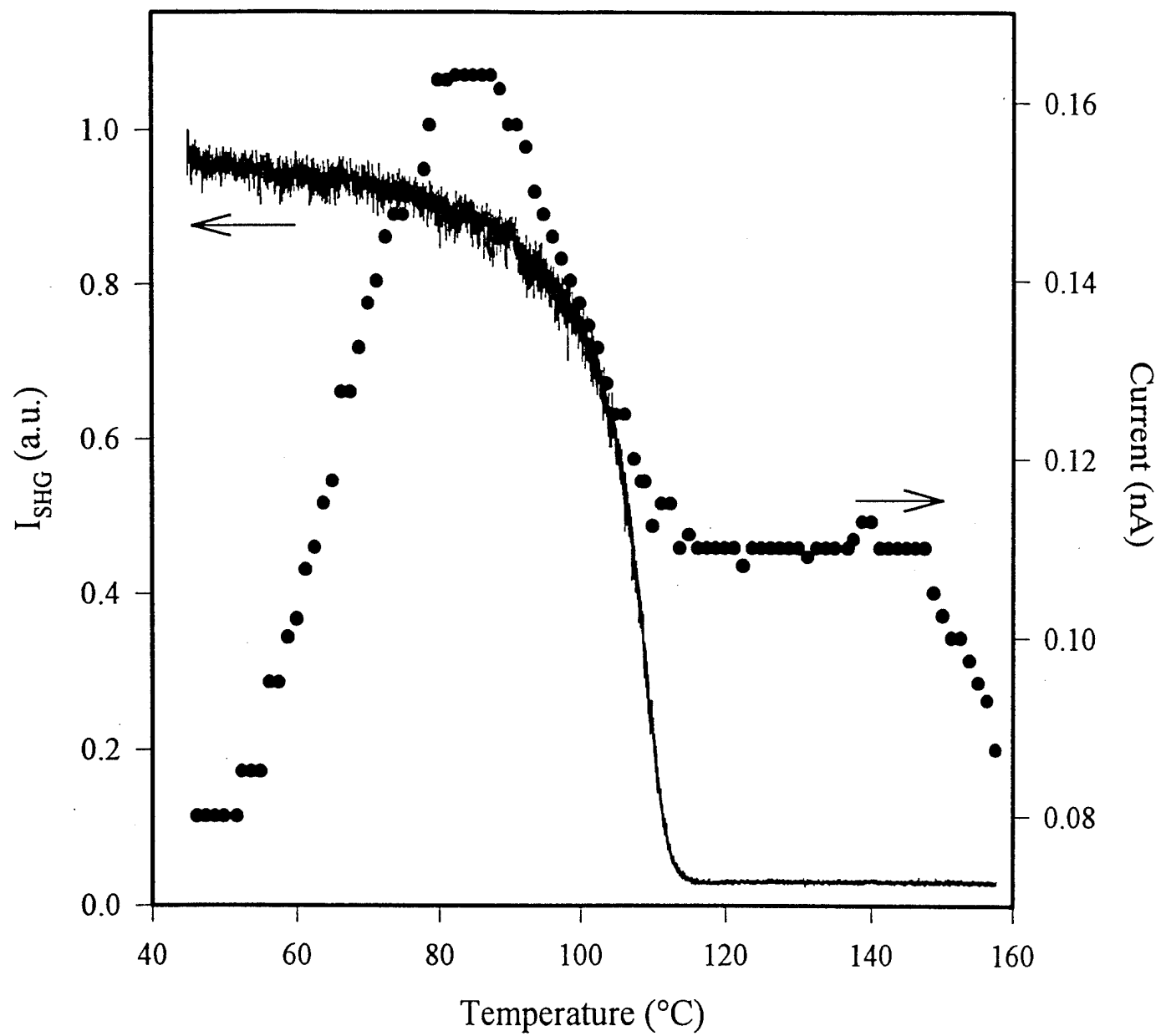


Figure 8, M. A. Pauley, *Macromolecules*

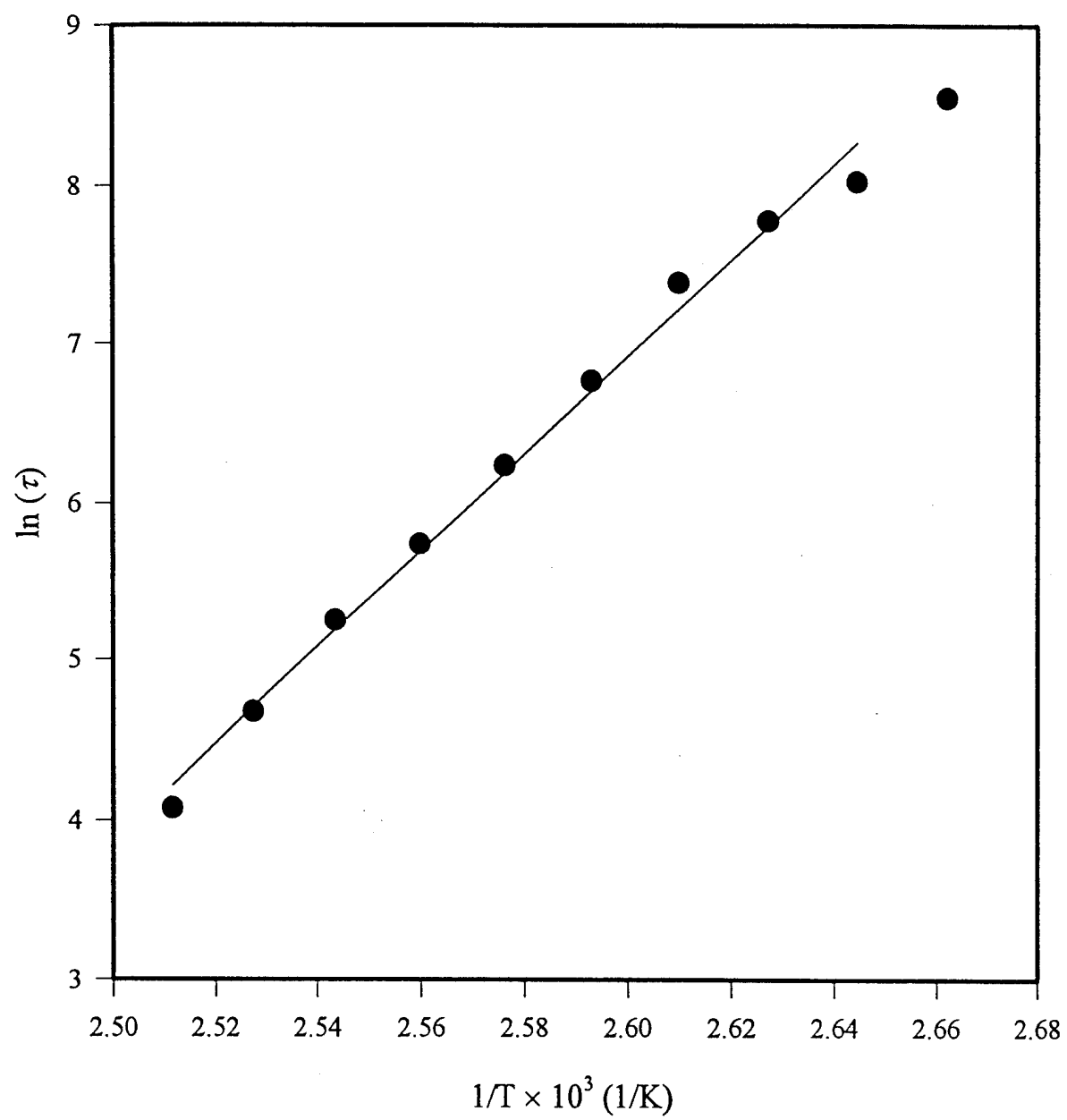


Figure 7, M. A. Pauley, *Macromolecules*

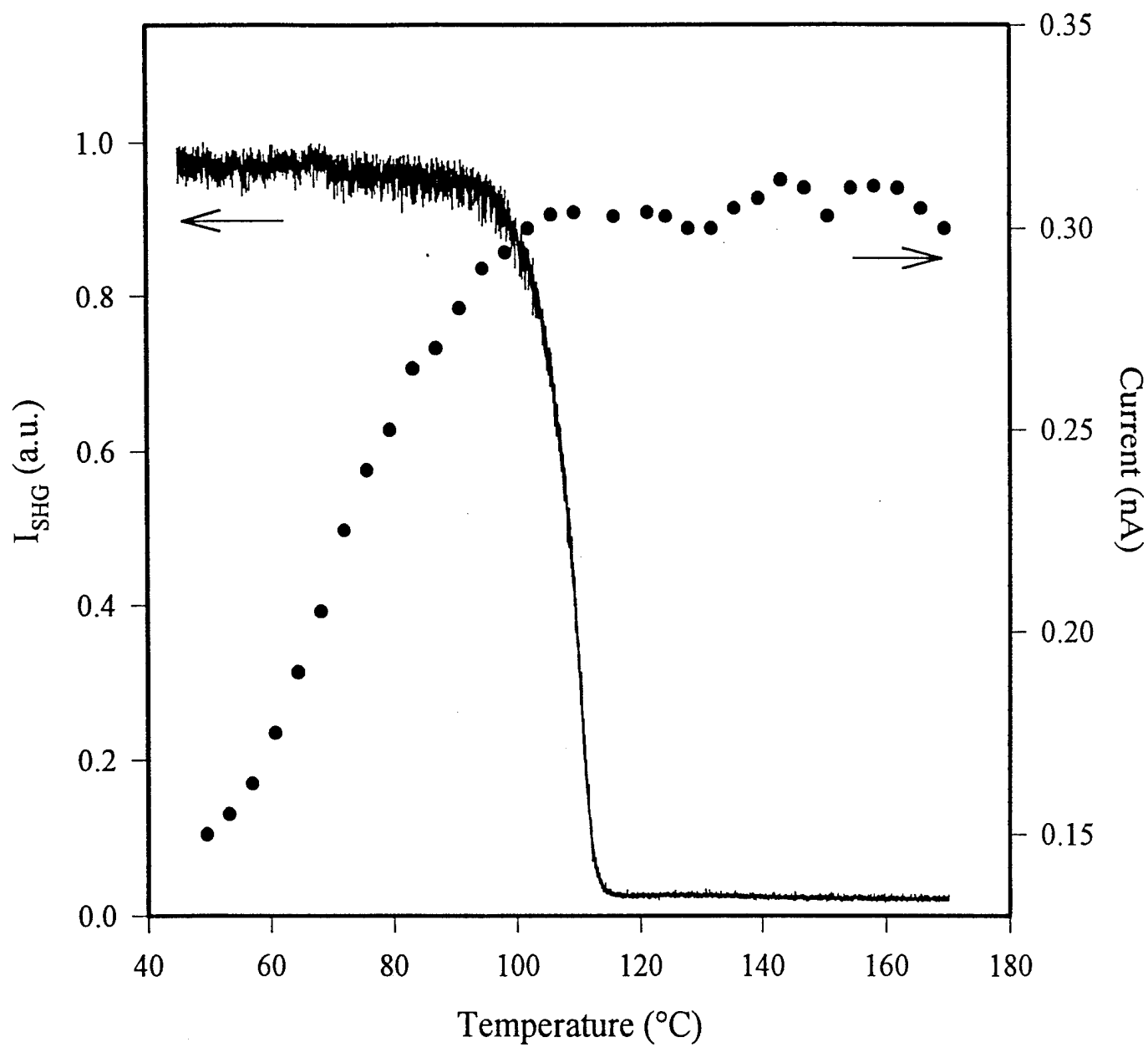


Figure 9, M. A. Pauley, *Macromolecules*